

## Feature Article

## Advances in polycarbodiimide chemistry

Justin G. Kennemur, Bruce M. Novak\*

Department of Chemistry, North Carolina State University, USA

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## ABSTRACT

Over the last 15 years, large strides have been taken with regards to synthesis, catalysis, structural control, and functional application of polycarbodiimides (polyguanidines); a unique class of helical macromolecules that are derived from the polymerization of carbodiimide monomers using transition metal catalysis. This manuscript will provide a summary of the synthesis and characterization studies in addition to the large variety of properties discovered for these systems and potential applications associated with these properties. In large part, it is the chiral helical backbone coupled with synthetically selective pendant groups which has allowed creation of polycarbodiimides spanning a large range of potential applications. Such applications include cooperative chiral materials, liquid crystalline materials, optical sensors and display materials, tunable polarizers, sites for asymmetric catalysis, and recyclable polymers. Manipulation of the two pendant groups that span away from the amidine backbone repeat unit has allowed solubility of these polymers in solvents ranging from cyclohexane to water, maximizing the potential application of these polymers in various media.

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## 1. Introduction

Before discussing the chemistry of these polymer systems, it is first necessary to clarify some of the confusions associated with their identification. In literature, the name polycarbodiimide is shared between the polymers of which this manuscript will review and the linear polycarbodiimides derived from diisocyanates which have garnered much attention for their dopant stabilization, cross-linking, and dehydration applications [1–11]. The reader should know that the latter linear polycarbodiimides are not discussed within this text. We refer to our systems as polycarbodiimides in a traditional sense since they are derived from carbodiimide monomers. The backbone of these polymers contains a repeating amidine or fully substituted guanidine-like structure and previous literature has attempted to rectify confusion by naming these systems polyguanidines. However, we feel this name is also misleading since the backbone nitrogens are not planar and are fully substituted, thus removing typical properties that are often associated with the guanidine or guanidinium moiety. For the purpose of consistency and simplicity we will continue to refer to our polymer systems as polycarbodiimides throughout this text but

further specificity will require their full description as non-linear or helical polycarbodiimides.

In 1964, Robinson first reported anionic low molecular weight polymerization of a variety of dialkyl-, diaryl-, and diallyl-carbodiimides using *n*-butyllithium catalyst [12]. Radical and cationic polymerization attempts were deemed unsuccessful. Thermal polymerization of diethylcarbodiimide at temperatures between 115 °C and 125 °C was also reported but only modest yields (~50%) were obtained after a period of 30 h and product was also deemed low in molecular weight [12]. Due to the lack of control over the polymerizations and the relatively low molecular weight obtained, no further work was reported. It wasn't until 1994 when Goodwin et al. reported the ability to polymerize carbodiimides in a living fashion through the use of organotitanium (IV) catalysts [13]. Patten et al. had previously proven these catalysts to be successful for controlled living polymerizations of isocyanates which are isoelectronic with carbodiimides [14]. The discovery of synthesizing polycarbodiimides in a living fashion was monumental due to the potential properties that these polymers may obtain.

One of the most prolific properties of polycarbodiimides is their asymmetric backbone which allows the formation of excess helical sense and/or chiral polycarbodiimides. Over the last thirty years, the field of synthetic helical polymer chemistry has taken tremendous strides after large potential was realized in such research during the early 1950's. It was during this time when the combined efforts of Pauling, Watson, and Crick revealed the helical macrostructures of proteins and DNA [15,16] and this revelation

\* Corresponding author. Postal address: Dabney Hall, 2620 Yarbrough Dr., Box 8204, Raleigh, NC 27695, USA. Tel.: +1 919 515 2996; fax: +1 919 513 2828.

E-mail addresses: [jgkennem@ncsu.edu](mailto:jgkennem@ncsu.edu) (J.G. Kennemur), [bmnovak@ncsu.edu](mailto:bmnovak@ncsu.edu) (B.M. Novak).

was soon followed by the discovery that helical polymers could be synthesized in a laboratory when, in 1955, Natta revealed that stereo-regular isotactic polypropylene exhibits a helical structure in the crystalline solid state [17]. Since that time, further understanding of the advanced functions governed by biological helices has propelled research into a variety of synthetic helical polymers designed for frontier applications. These polymers presently encompass an assortment of carbon and heteroatom-based backbones synthesized from an even larger variety of catalysts. An in-depth review of the current advances in chiral macromolecular design lies outside the scope of this manuscript, however, the reader is encouraged to refer thorough and well written reviews of this subject and the references therein that have been previously published [18–39]. Relevant advances as they pertain to helical polycarbodiimide chemistry will be discussed *vide infra*.

### 1.1. Catalysis of polycarbodiimides

Since the discovery of **Cat-1–3** (Fig. 1) and their ability to polymerize carbodiimides in a living fashion [13], a variety of titanium, copper [40], nickel, and zirconium catalysts [41] have been synthesized (Fig. 2). The titanium (IV) catalysts are air and moisture sensitive requiring the use of a Schlenk apparatus under an inert nitrogen blanket or an inert dry box system for synthesis and polymerizations. The amine and alkoxide ligands that originate on the titanium center are known as the initiation or transfer ligands. Upon initial coordination of the first carbodiimide nitrogen onto the titanium metal center, this ligand transfers onto the electrophilic center carbon of the carbodiimide (Scheme 1). As the polymerization progresses and sequential carbodiimides insert, the initiator ligand remains on the polymer as an end group while the rest of the catalyst carries along the propagating chain end. The retained ligands on the metal center can be chiral or achiral and their size and inductive effects can greatly alter the kinetics of polymerization. The 1,1'-binaphth-2,2'-ol (BINOL) ligand was employed as a chiral ligand for titanium catalysts to induce helix-sense-selective polymerization of achiral carbodiimides. Due to the atropisomeric nature of the BINOL ligand, they can be designated as R (**Cat-4,6**) or S (**Cat-5**) and racemization of the ligand by rotation of the aryl–aryl bridging bond does not occur at modest temperatures due to steric inhibition. (R)-BINOL titanium diisopropoxide (**Cat-4**) and its (S) enantiomer (**Cat-5**) have been shown to successfully polymerize many different symmetric and non-symmetric carbodiimides into an excess helical sense [42–49]. Due to known aggregation of these plain BINOL based titanium catalysts [50],

many of the bulkier BINOL based catalysts (**Cat-7–10**) were synthesized to reduce aggregation [42,43]. This is also the reasoning behind using bulkier alkoxide initiator ligands such as isopropoxy (**Cat-4,5,8**) or *tert*-butoxy (**Cat-6,7,9**).

Of the BINOL catalysts made, only **Cat-7, 9**, and **10** were found to be monomeric as a solid crystal, the most notable being **Cat-7** due to its moderate activity and good yields of resulting polymer [42,43]. Even though crystals of these catalysts are shown to be monomeric, aggregation behavior may be different when dissolved in various solvents. The tridentate BINOL based titanium(IV) catalysts (**Cat-11–14**) were made in an effort to maximize helix-sense-selective polymerization however reaction times were very slow and resulting polymers were of low yield ( $\leq 36\%$ ) and likely low in molecular weight [43]. The general trend is that bulky BINOL ligand based titanium catalysts are less aggregated but, as a consequence, polymerize carbodiimides much slower. Additionally, if the carbodiimides themselves have bulky pendant groups, polymerization may not occur at all. The achiral trichlorotitanium(IV) trifluoroethoxide catalyst (**Cat-15**) is a highly active catalyst. The three chloride ligands are less bulky than BINOL ligands and they also increase the activity of the titanium center by inductively withdrawing electron density. As a result, **Cat-15** allows fast, controlled polymerizations and provides high polymer yields [46]. Consequently, since there is no chiral influence from this catalyst, it is not a candidate for helix-sense-selective polymerization of achiral monomers.

Cationic dicyclopentadienyl-methyl zirconium(IV) catalyst with a large chiral tris(tetrachlorobenzene diolato)phosphate(V) counter anion (**Cat-24**) has shown some initial success toward zirconium based polymerizations [41]. The larger metal center belongs to the same periodic group as titanium and was shown to also successfully polymerize achiral symmetric and asymmetric carbodiimides such as *N*-(methyl)-*N'*-(phenyl) carbodiimide (92% yield of polymer reported) [51]. The large chiral anion was designed to govern the direction of insertion and propagation of the polymer chain and achieve helix-sense-selective polymerizations but this was deemed unsuccessful.

Due to the challenges of handling air and moisture sensitive catalysts, copper(I/II) catalysts, having late transition metal centers, were synthesized to provide a more robust route of creating polycarbodiimides. Initial experiments using common copper(I) (**Cat-16**) and copper(II) (**Cat-17,18**) salts showed promise for polymerizing carbodiimides under normal atmosphere with the copper(II) salts showing greater activity [40]. Further improvements to the design yielded copper(II) amidinate complexes (**Cat-19–21**) and

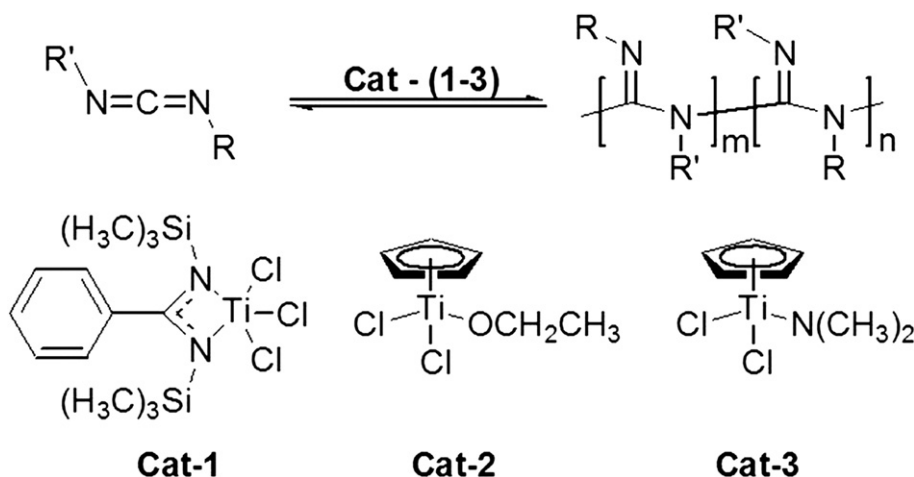


Fig. 1. Initially discovered titanium(IV) catalysts, **Cat-(1–3)**, shown to polymerize carbodiimides in a living fashion [13].

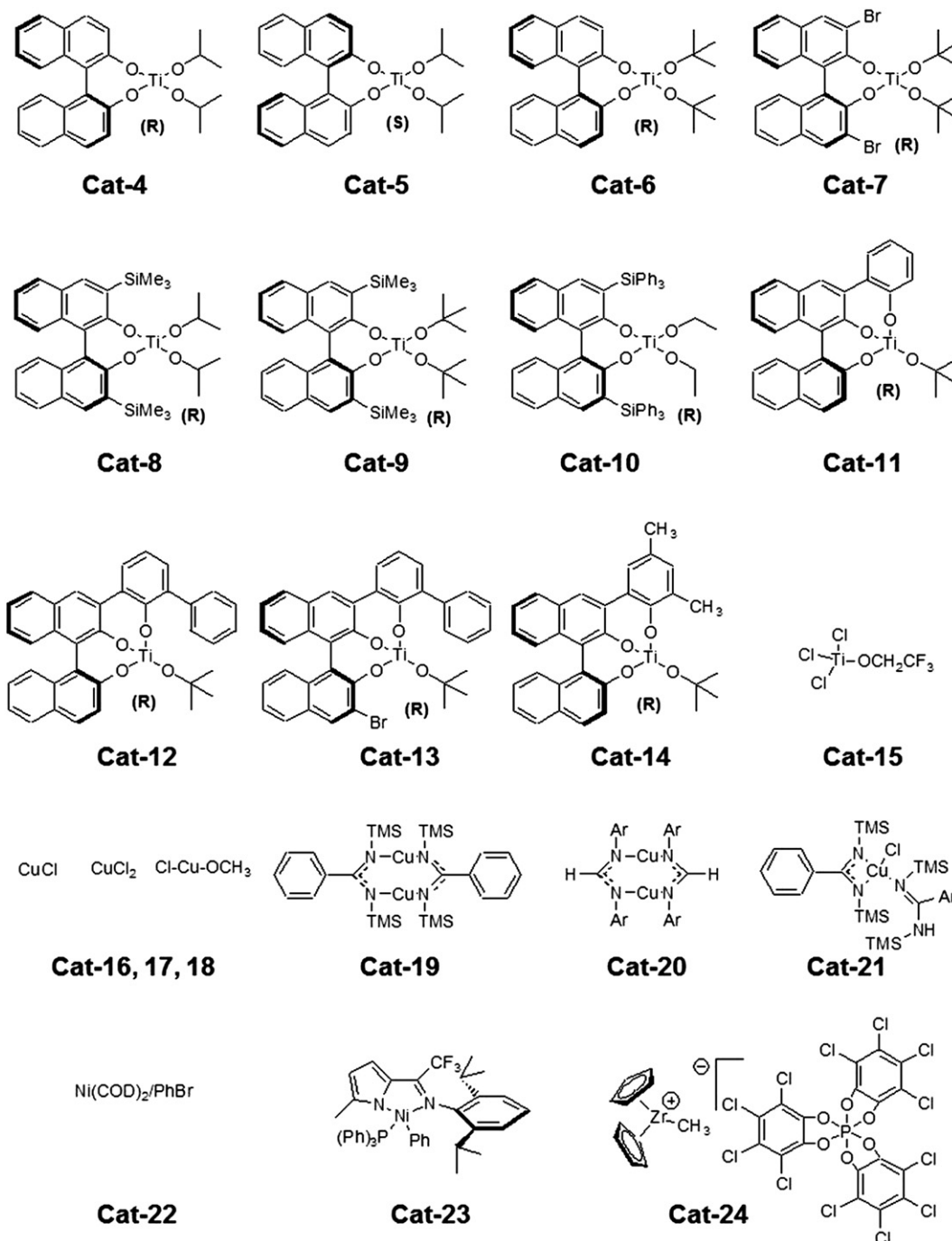
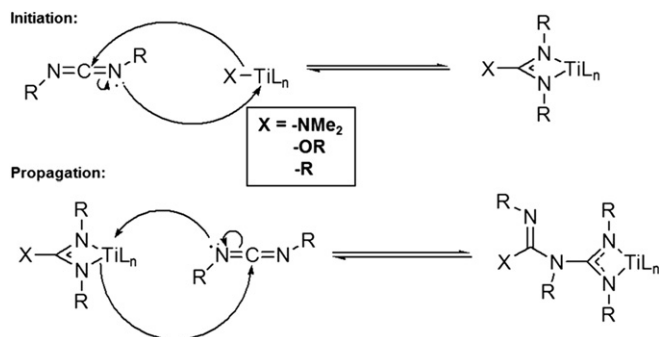


Fig. 2. List of catalysts capable of polymerizing carbodiimides.

resulted in yields equivalent to those observed for titanium(IV) complexes [40]. These catalysts have good tolerance in air and in minimally wet solvents, although using excessive water was shown to reduce the yield of polymer. These systems were also shown to be living due to the absence of chain transfer and chain termination side-reactions. Drawbacks to these copper catalyst systems include stubborn solubility of the copper salt complexes in most solvents and the absence of chiral ligands capable of helix-sense-selective polymerization. Unreported preliminary experiments with nickel based catalyst systems (**Cat-22,23**) were also found to tolerate oxygen and moisture and reasonably high yields of polycarbodiimide were obtained but without the ability for excess chiral induction.

To date, titanium catalysts have provided the bulk of carbodiimide polymerizations reported. Different polymerization conditions using different monomers and a variety of the aforementioned catalysts have shown improvements to specific polymerization systems. Collectively, there is still much to learn about the behavior of these polymerizations. As a result of the equilibrium process, monomer reversibly coordinates and inserts during propagation. For this reason many polymerization trials were performed neat (no solvent) using various liquid monomers. Le Chatelier's principle suggests that increasing monomer concentration drives the equilibrium toward polymer formation. The use of solvent would decrease monomer concentrations and therefore polymer yields would suffer. Although this is true in theory, it is typically found that



**Scheme 1.** Initiation and propagation mechanism for the polymerization of carbodiimides using a titanium(IV) catalyst.

higher yields and better polymer solubilities are obtained from polymers that are created in the presence of a small amount of solvent ( $\sim 1$  mL per gram of monomer) such as chloroform. Neat polymerizations can be wrought with other inconsistencies; the most prominent being the potential inability for monomer to act as a proper solvent for the catalyst. Pre-dispersing the catalyst in a small amount of solvent prior to polymerization can provide a better homogeneity of the polymer initiation process and allow better mobility of monomer to propagate onto the chain as polymerization progresses. Additionally, solvent must be used if the monomer is a solid. Other fluctuating experimental conditions such as the purity and composition of the monomer, the polymerization temperature, and the monomer to catalyst ratio can collectively affect the polymer outcome as well. Many of the more advanced BINOL based titanium (IV) catalysts have not taken into account these other variables that may play a large role on the properties of the resulting polymers. Conducting a series of experiments that systematically takes into account every one of these variables would be a very large task; however, it is important moving forward that one keeps awareness of these variables.

## 1.2. Carbodiimide monomers

Before discussing polycarbodiimides, it is first important to gain a fundamental understanding of their monomer precursors. Carbodiimides are the diimides that in principle are derived from carbon dioxide and have a heterocumylene structure that is isoelectronic with isocyanates [52]. The two nitrogen-attached pendant groups can be identical (symmetric carbodiimides) or different (non-symmetric carbodiimides) and may be of a wide range of functionalities including alkyl, aryl, acyl-, trimethylsilyl-, thioacyl-, imido-, or even halogens. Commercially, only a small set of carbodiimides are available and these reagents are often used as mediators in peptide, nucleotide, and, more recently, proteomics chemistry [52]. They are also valuable dehydration agents due to their ability to form stable and often insoluble ureas which can easily be removed by filtration [52]. Other uses for carbodiimides include polymer additives, heterocycle synthesis, permease inhibition, and cycloaddition reactions [53]. All of the carbodiimide monomers used in this manuscript are not commercially available and therefore continual synthesis and purification improvements, as well as the understanding of the stability of this particular class of molecules are the continual result of this research.

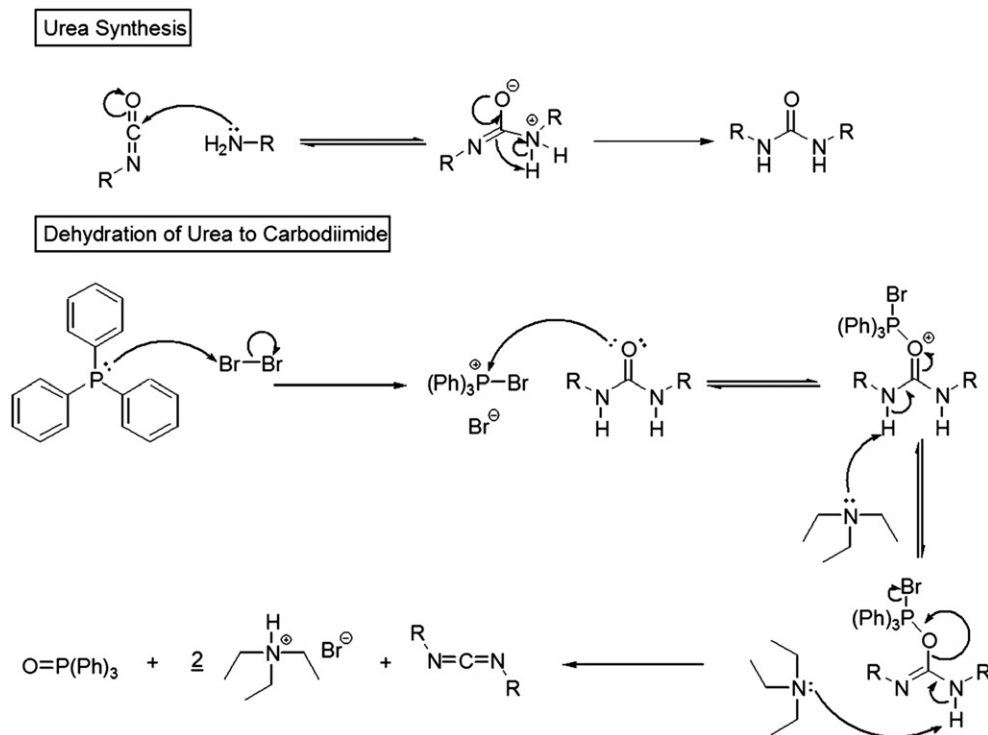
Due to their allene structure, carbodiimides can exist as stereoisomers, but only a few carbodiimides have ever been resolved into their existing enantiomeric forms. One such example, bisferrocenylcarbodiimide, has been partially resolved and it is claimed that a stabilizing interaction between the ferrocenyl groups and the

carbodiimide moiety is the reason for this resolution [53]. However, most carbodiimides are not resolvable due to a very low-energy barrier to racemization of the carbodiimide through imine inversion and rotation which has been calculated to be  $< 10$  kcal/mol by a semi-empirical method [53]. Due to these low-energy isomerizations, we refer to any carbodiimide monomers without an actual stereogenic center to be considered achiral, however, the reader should be aware of the general asymmetry associated with the carbodiimide itself. Symmetric carbodiimides are generally easier to synthesize over non-symmetric derivatives. Traditionally, primary amines can be combined with a coupling agent such as phosgene, triphosgene, or bis-(4-nitrophenyl) carbonate followed by dehydration of the subsequent 1,3-disubstituted urea. Another way to prepare symmetric carbodiimides is from isocyanates using a phospholene oxide catalyst which requires no solvent and this method generally produces good yields due to the production of carbon dioxide, which drives the reaction [54]. Alternatively, thioureas can be synthesized followed by desulfurization using mercuric oxide. This was the method used by Robinson during his initial success with carbodiimide polymerization [12].

For many cases, our research progress has employed non-symmetric carbodiimides due to the inherent diversity that the two different pendant groups can give to the polymer system. The synthesis of choice involves the reaction of a primary amine and an isocyanate to form a 1,3-disubstituted urea (Scheme 2). Very often, the urea product has stubborn solubility due to the inherently polar urea moiety and the relatively non-polar nature of the pendant groups chosen. Dehydration of a urea slurry in dichloromethane using dibromotriphenylphosphorane, a salt adduct that can be made in-situ by the addition of molar equivalents of bromine and triphenylphosphine, and 2 M equivalents of an acid scavenger such as triethylamine (TEA) yields the carbodiimide product along with triphenylphosphine oxide and triethylammonium bromide by-products.

Optimal purification of the carbodiimides following dehydration is an ongoing process and requires constant adjustment depending on the nature of the nitrogen-attached pendant groups. Purchase of pre-made dibromotriphenylphosphorane salt has eliminated some of the more persistent contaminants which are believed to originate from uncomplexed bromine reagent used to make the salt in-situ. Other ways of synthesizing non-symmetric carbodiimides include reaction of isocyanates with iminophosphoranes via the aza-Wittig reaction [55] or with phosphoramidates [56], and the use of amidoximes via the Tiemann rearrangement [57]. For symmetric carbodiimides, final purification by vacuum distillation is the preferred method provided that the monomer has a low enough boiling point. This method is not recommended for non-symmetric carbodiimides due to their ability to thermally metathesize, a process by which two carbodiimides dimerize and exchange pendant groups leading to a mixture of symmetric and non-symmetric carbodiimides. Our work has found that this metathesis is more favorable with non-symmetric carbodiimides containing an aryl and an alkyl pendant group. Instead, we have achieved success purifying these non-symmetric carbodiimides through column chromatography using neutral pH silica gel.

The storage and stability of carbodiimides can fluctuate depending of the nature of the pendant groups. Bulky tertiary alkyl pendant groups typically provide the best stability for carbodiimides due to their size and the relatively inert induction effects of hydrocarbons on the carbodiimide moiety [52]. Later it will be shown that bulky tertiary and secondary alkyl groups are not ideal for the synthesis of polycarbodiimides due to steric limitations. Aryl groups tend to lend instability to carbodiimides especially if they contain electron donating groups in the ortho- or para-position. This instability is not necessarily a bad thing because it is directly



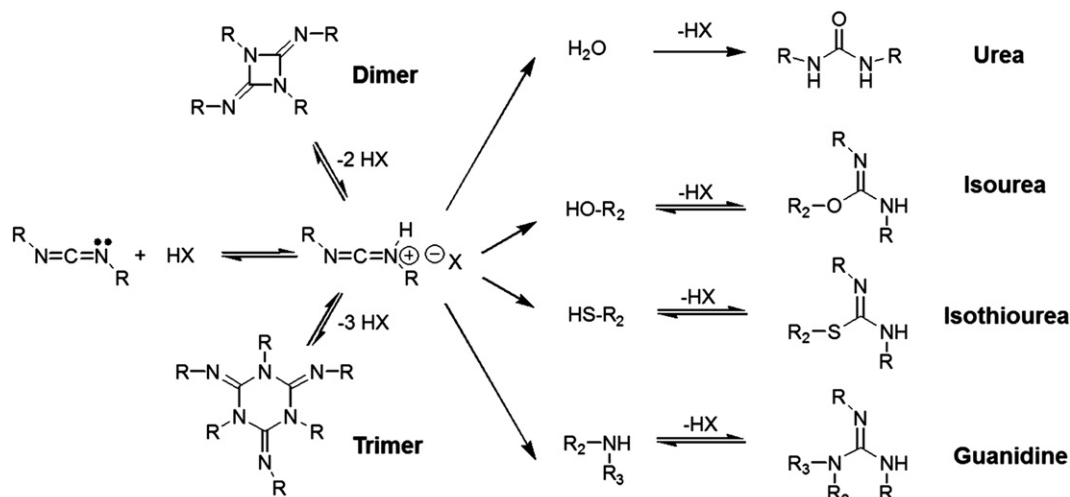
**Scheme 2.** Synthesis of carbodiimides by the reaction of a primary amine and an isocyanate followed by subsequent dehydration of the 1,3-disubstituted urea using dibromotriphenylphosphorane and an acid scavenger triethylamine.

correlated to their reactivity and, therefore, their ability to be polymerized quickly. Other trends state that solid carbodiimides are more stable than liquid and that diarylcarbodiimides are more stable than *N*-alkyl-*N'*-aryl carbodiimides [52]. Most of the carbodiimide monomers discussed herein can be dried and stored under nitrogen atmosphere at cold temperatures and remain stable for at least a few weeks prior to polymerization. Carbodiimides that are solid at the storage temperature have been stored for months without any appreciable degradation.

Carbodiimides will react rapidly in the presence of acid to form cyclic dimers and trimers (Scheme 3). Protonation of the basic carbodiimide nitrogen catalyzes their reactivity allowing the electrophilic

carbon center to be highly susceptible to nucleophiles. In the presence of water and acid, carbodiimides will convert back to their stable urea precursors. Without water, other nucleophiles such as alcohols, thiols, and amines will react to form isoureas, isothiureas, and guanidines respectively.

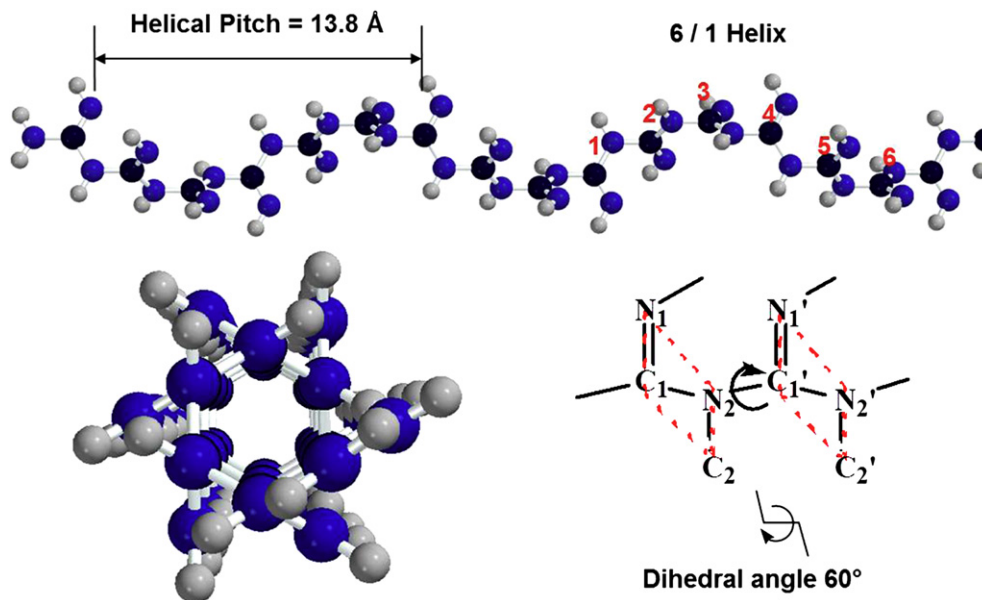
With this in mind, it is important for our monomers to be void of any acidic protons prior to polymerization. Care must be taken when purifying monomers using column chromatography on silica gel due to residual acid and water that is adsorbed on the silicon oxide surface. Although resulting ureas are usually insoluble in the mobile phase and are retained on the column, neutral silica gel (pH = 7.0) is recommended to minimize loss of carbodiimide product.



**Scheme 3.** Carbodiimides are unstable in the presence of acid which catalyzes a series of reactions based on the nucleophiles present. The presence of acid alone catalyzes the formation of dimers and trimers.







**Fig. 5.** Molecular mechanics and modeling results of a simple, dimethyl polycarbodiimide backbone reveals a 6/1 helical sense with a helical pitch of 13.8 Å and a dihedral angle of approximately 60° between repeat units.

Through molecular mechanics and modeling of these systems, the dihedral angle between repeat units is approximately 60°, however this is likely to fluctuate depending on the bulk of the pendant groups. For example, di-*n*-hexyl polycarbodiimide (**Poly-6**) is calculated to have a 55° dihedral angle while *N*-methyl-*N'*-((*R*)-1-phenylethyl) polycarbodiimide (**Poly-2**) is calculated to have a dihedral angle of 74°. Additionally, the helical pitch, or the distance between identical places on neighboring helical turns, can fluctuate with bulkier pendant groups but is generally calculated to be around 13.7 Å. It takes approximately six repeat units to make one complete helical turn, hence, polycarbodiimides adopt a 6/1 helix. Another interesting feature of the polycarbodiimide backbone is its polarity. Due to the imine lone pairs along the backbone and their ability to form an all syn structure with bulky substituents, this polarity aligned in a vector that travels down the axis of the helix can have an additive dipole of up to 1.7 debyes/repeat unit as calculated at the semi-empirical AM1 level.

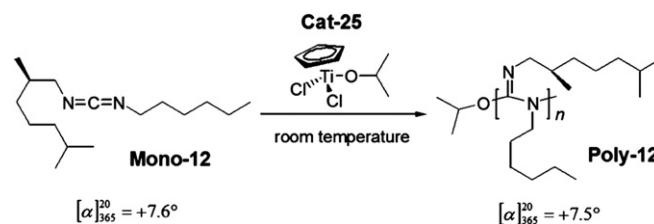
As stated, the ability to choose between two different pendant groups per unit on the repeating amidine backbone is a key feature for polycarbodiimides and offers a new level of synthetic versatility when compared to their helical polymer counterparts. In addition to the helical pitch and the dihedral angle between repeat units, the two pendant groups ultimately define some of the major properties of these polymer systems; the helical inversion barrier, solubility, liquid crystalline behavior, and regioregularity of these polymer systems can all be dictated by the choice of pendant groups.

### 2.2.1. Polycarbodiimides as dynamic helical polymers

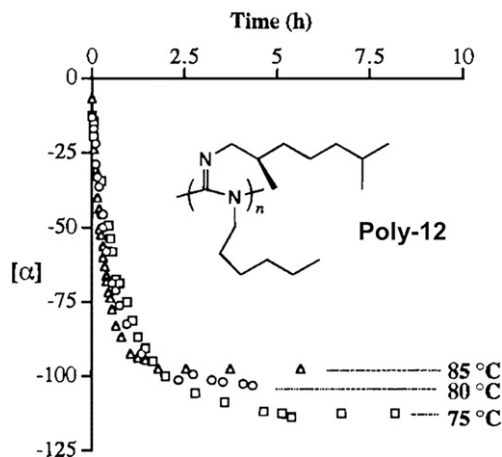
Dynamic helical backbones are defined by relatively low-energy helical inversion barriers and backbones that can adopt an excess helical sense with moderate to high cooperativity through use of a chiral influence [18]. Classical experiments such as sergeants-soldiers [62], majority rules [59,77], and molecular chaperones [104,105] have been used to exemplify this cooperativity. Such experiments have been attempted with polycarbodiimides and many of these experiments have led to mixed but interesting results.

To begin understanding the nature of the polycarbodiimide backbone, experiments involving induction of an excess helical sense were initiated. In 1998, Schlitzer reported an experiment by

polymerizing the chiral *N*-(*R*)-2,6-(dimethylheptyl)-*N'*-(*n*-hexyl) carbodiimide (**Mono-12**) using cyclopentadienyl-dichloro-titanium(IV) isopropoxide catalyst (**Cat-25**, Scheme 4) [106]. The achiral catalyst was found to polymerize **Mono-12** into a kinetically controlled conformation (KCC) as evidenced by the polymer adopting no more specific optical rotation than that observed from the monomer. By annealing the polymer at temperatures of 75, 80, and 85 °C, a large amplification in specific optical rotation from  $[\alpha]_{365} = +7.5^\circ$  to  $[\alpha]_{365} = -157.5^\circ$  in hexane ( $c = 0.24$  g/100 mL) occurred which eventually plateaus off (Fig. 6). This increase in optical rotation can be explained by the fact that the initial KCC of the polymer was an equal mixture of left and right handed helical segments with a diastereomeric relationship due to the homochiral pendant group. Upon heating at higher temperatures, the relatively non-bulky pendant groups allowed inversions of the backbone to become possible and **Poly-12** was able to adopt a thermodynamically controlled conformation (TCC) and the preferred lower-energy helical sense. The process was not reversible and the energy barrier to helical inversion was initially reported as 6.4 kcal/mol [106] but was later corrected and determined to be approximately 21.6 kcal/mol. **Poly-12** is an example of how polycarbodiimides can behave as dynamic helical polymers when the pendant groups are relatively free from steric crowding. Tian and Lu et al. later performed a similar experiment using *N*-(*R*)-2,6-dimethylheptyl-*N'*-phenyl polycarbodiimide **Poly-13** from **Cat-15** and discovered that an even greater amplitude in optical rotation is seen when using an aromatic pendant group (Fig. 7) [44].



**Scheme 4.** The chiral **Mono-12** is polymerized kinetically by **Cat-25** resulting in **Poly-12** with no excess helical sense and a specific optical rotation equivalent to that of the starting monomer.



**Fig. 6.** Annealing of **Poly-12** at 85, 80, and 75 °C allows the polymer to adopt the thermodynamically preferred helical sense and results in a large increase in optical rotation. (Copyright 1998 American Chemical Society, reprinted with permission) [106].

Interestingly, the initial polymer prior to annealing is already found to have a large optical rotation  $[\alpha]_{435} = -209^\circ$  and during the annealing process the optical rotation permanently changes to a large value in the opposite direction  $[\alpha]_{435} = +255^\circ$ . This was also ascribed to be a transition from KCC to TCC and the energy barrier to helical inversion was reported as 29.2 kcal/mol [44]. This increase in helical inversion energy is a testament to the relationship between steric crowding of the aryl group on **Poly-13** compared to the hexyl group on **Poly-12**. An interesting observation is that the final specific optical rotations after annealing of **Poly-12** ( $-157^\circ$ ) and **Poly-13** ( $+255^\circ$ ) are in opposite rotatory directions even though the chiral pendant group for both is the same.

Due to the repeating amidine backbone and the relative basicity of the nitrogens, one can expect the addition of acid to protonate the backbone of these polymers if the pendant groups are not too bulky and the counter anion can be electrostatically held in proximity of the protonated nitrogen. Taking advantage of this property, another experiment reported by Schlitzer was done on di-*n*-hexyl polycarbodiimide (**Poly-6**) which was polymerized into a racemic KCC using achiral **Cat-25** [106]. Unlike **Poly-12**, this polymer has no configurationally chiral pendant group and therefore annealing will not promote the formation of a diastereotopic excess helical sense. Instead, a molecular chaperone experiment was performed to induce an excess helical sense by protonation of the backbone with chiral (*S*)-camphorsulfonic acid ((*S*)-CSA) (Fig. 8a). As the molar

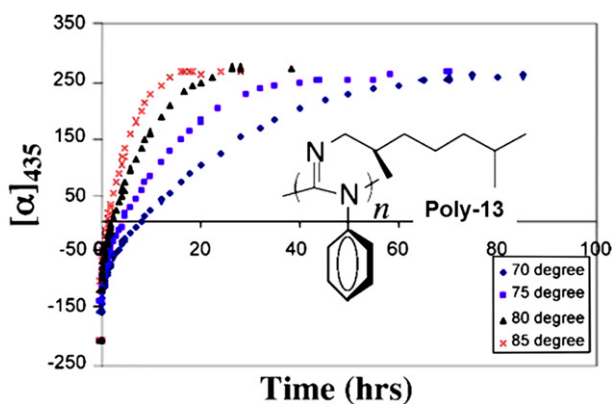
equivalents of (*S*)-CSA were increased, a non-linear increase in specific optical rotation was observed for **Poly-6** (Fig. 8b). (*R*)-CSA caused mirror image behavior and optical rotation to increase in the opposite direction. Mild heating and changing the polarity of the solvent was also found to increase the effectiveness of this induction. Although it was concluded that protonation with a chiral acid can induce an excess helical sense, the cooperativity of polycarbodiimides requires a 4:1 (mol. repeat unit:mol. acid) ratio before significant increases in specific optical rotation is observed. It is speculated that an expansion of the helical pitch of the polycarbodiimide backbone occurs when protonated due to electrostatic repulsions of the positively charged nitrogens and this may account for the general lack of cooperativity.

Preliminary studies on cooperative behavior (sergeant-soldier, majority rules) in addition to the aforementioned chiral acid study has allowed us to make some conclusions about the dynamic behavior of polycarbodiimides; (1) they can behave as dynamic helical polymers when using relatively non-bulky pendant groups, (2) some evidence of cooperativity is seen in these systems with sergeant-soldier, majority rules and molecular chaperones experiments but due to differences in polymerization kinetics between co-monomers (two sterically different carbodiimide monomers), backbone conformational restrictions, and potential regioirregularity between backbone repeat units, these systems are currently unable to exhibit high cooperativity, (3) in addition to the  $\alpha$ -position, configurationally chiral stereocenters on the  $\beta$ -position of alkyl pendant groups are of adequate proximity to influence the helical sense of the backbone, (4) arene pendant groups can often lead to enhanced optical rotations, and (5) the basicity of the polymer backbone allows sufficient protonation from organic acids and the use of chiral counter-anions can induce an excess helical sense. These experiments are worth revisiting once better control and understanding of the polymer macrostructure is obtained.

### 2.2.2. Polycarbodiimides as static helical polymers

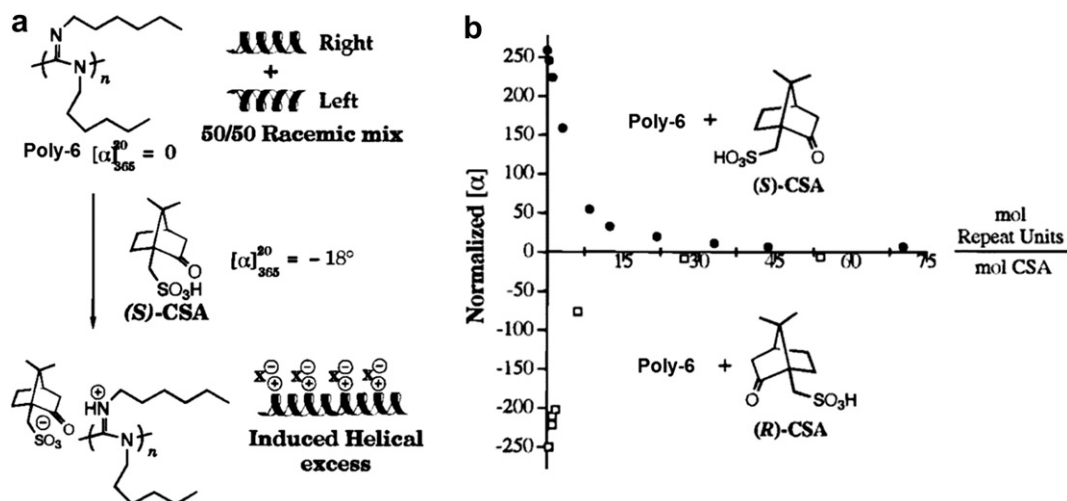
The use of chiral pendant groups to obtain an excess helical sense can be costly and time consuming to synthesize. New focus was placed on creating polycarbodiimides through helix-sense-selective polymerizations using chiral catalysts with achiral monomers from cheaper and readily available precursors. As previously stated, chiral BINOL titanium(IV) catalysts allow achiral monomers to be polymerized into a preferred excess helical sense. The goal is to synthesize monomers that will incorporate sufficient steric hindrance to prevent main chain bond rotations and yield robust helical polymers with an appreciably high energy barrier to racemization. A problem becomes apparent when observing the initial polymerizations performed in Section 2.1. Increasing the bulk of the pendant groups too much will result in no polymerization (**Mono-(9–11)**). However, when comparing the aliphatic pendant group containing **Poly-12** ( $E_r = 21.6$  kcal/mol) discussed in the previous section, a higher energy helical inversion barrier was observed for **Poly-13** ( $E_r = 29.2$  kcal/mol) due to the phenyl pendant group. Building upon this observation, the idea of adding restrictive substituents to the phenyl group led to a new family of polycarbodiimides that were designed with the intention of creating static helical polycarbodiimides.

Lim and Kim et al. synthesized a series of polymers using **Mono-6,14–17** (Fig. 9) with **Cat-3** and observed their  $^{13}\text{C}$  spin-lattice relaxation times in the rotating frame as a function of temperature using solid state  $^{13}\text{C}$  cross-polarized/magic angle spinning (CP/MAS) NMR spectroscopy [107–110]. From these experiments, the relative rigidity of the backbone can be calculated by determining the activation energies of the imine carbons for each polymer (Table 1). When comparing the results to the base di-*n*-hexyl **Poly-6** (19.76 kcal/mol), the diaryl pendant polymers **Poly-14** and **Poly-**



**Fig. 7.** Annealing **Poly-13** results in a redirection in optical rotation by evolving from its KCC to its TCC at various temperatures in toluene ( $c = 0.2$  g/100 mL). (Copyright 2004 American Chemical Society, reprinted with permission) [44].



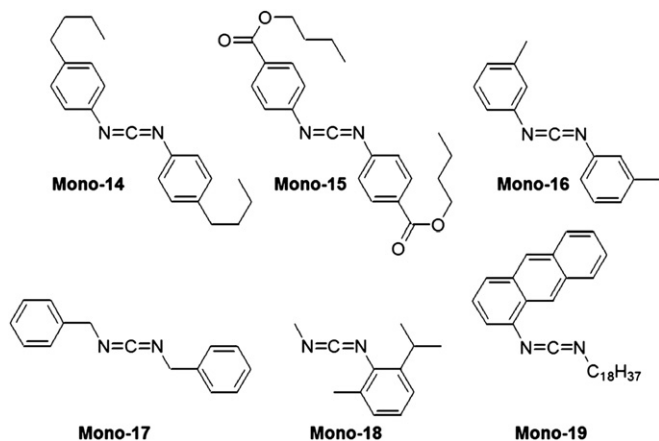


**Fig. 8.** (a) Chiral acids can function as molecular chaperones and induce an excess helical sense to a racemic mixture of polycarbodiimides containing no chiral pendant groups. (b) Mirror image optical rotation behavior is seen by using enantiomeric acids. (Copyright 1998 American Chemical Society, reprinted with permission) [106].

**16** had a higher energy barrier of 23.20 and 23.12 kcal/mol respectively. Interestingly, the di-(4-butoxycarbonylphenyl) **Poly-15** was calculated to have a lower-energy barrier of 18.63 kcal/mol. The di-benzyl **Poly-17** had the lowest energy barrier of them all at 12.64 kcal/mol. Since the imine carbon along the polymer backbone has no directly attached protons, their relaxation times can be very slow and were reported to be significantly broadened at higher temperatures. Coupling this with the fact that these carbons only comprise half of the backbone composition (the other half being the amine nitrogen), these results may not be a direct representation of the full dynamics involved in the racemization process. It is likely that full racemization of the polymer involves a combination of modes such as main chain bond rotations, pendant group rotations, and imine inversions.

A more inclusive way to determine the energy barrier to helix racemization ( $E_r$ ) is by annealing the polymer and observing the loss of optical rotation through the use of polarimetry. This system is modeled after the equation representing the two helical senses in a reverse equilibrium, Eq. (1), where  $[M]_0$  represents the initial concentration of the excess

$$\ln \left( \frac{([M]_0 - [M]_{eq})}{([M] - [M]_{eq})} \right) = k_{obs}t \quad (1)$$



**Fig. 9.** Achiral carbodiimide monomers designed to induce a large racemization barrier on resulting polymers.

helical sense,  $[M]_{eq}$  is the concentration at equilibrium,  $[M]$  is the concentration being observed as a function of time “ $t$ ”, and  $k_{obs}$  is the rate constant. Since we cannot directly measure the concentration of excess helical sense, we can replace it with the observed specific optical rotation,  $[\alpha]$ , which yields Eq. (2).

$$\ln \left( \frac{([\alpha]_0 - [\alpha]_{eq})}{([\alpha] - [\alpha]_{eq})} \right) = k_{obs}t \quad (2)$$

As discussed, it is thermodynamically favorable for the helix to completely racemize when polymerized from achiral monomers. Therefore, we can assume the specific optical rotation at equilibrium,  $[\alpha]_{eq}$ , to be zero since all the helical segments rotating in the positive direction are being canceled by an equal amount being rotated in the negative direction. Hence, Eq. (2) can be further simplified to Eq. (3). A linear plot using this equation will yield  $k_{obs}$  as the slope. By performing these experiments at different temperatures we can obtain multiple

$$\ln \left( \frac{([\alpha]_0)}{([\alpha])} \right) = k_{obs}t \quad (3)$$

rate constants and use them in the Arrhenius Eq. (4) to determine the energy barrier to racemization ( $E_r$ ) where  $T$  is the temperature in Kelvin and  $R$  is the molar constant. To obtain  $E_r$  in kcal/mol it is often typical that the x-axis be plotted as  $1/(T \times 1000)$ .

$$\ln(k_{obs}) = \left( \frac{E_r}{R} \right) \frac{1}{T} + \ln(A) \quad (4)$$

By using this method, Lu determined the  $E_r$  for **Poly-6** polymerized from **Cat-5** to be 22.8 kcal/mol, which is 3 kcal/mol

**Table 1**  
Backbone activation energy barriers of imine carbons on several polycarbodiimides obtained by  $^{13}\text{C}$  CP/MAS NMR spectroscopy.

Polymer ID	Pendant Group 1	Pendant Group 2	$E_a$ (kcal/mol)
<b>Poly-6</b>	n-hexyl	n-hexyl	19.76
<b>Poly-14</b>	4-butylphenyl	4-butylphenyl	23.20
<b>Poly-15</b>	4-butoxycarbonyl phenyl	4-butoxycarbonyl phenyl	18.63
<b>Poly-16</b>	3-methylphenyl	3-methylphenyl	23.12
<b>Poly-17</b>	benzyl	benzyl	12.64

higher than that reported by Lim and Kim using  $^{13}\text{C}$  CP/MAS NMR. *N*-hexyl-*N'*-phenyl polycarbodiimide (**Poly-20**) was also synthesized using **Cat-5** and the  $E_r$  determined as 25.6 kcal/mol [44]. This result reconfirms that aryl pendant groups result in improved helical stability when compared to primary aliphatic groups.

Further steric hindrance was induced by incorporating alkyl substituent on the ortho-positions of the phenyl pendant group. *N*-methyl-*N'*-(2-methyl-6-isopropylphenyl) polycarbodiimide (**Poly-18**, Fig. 10) was the most successful of these derivatives due to the polymerizability of the monomer (resulting from the other methyl pendant) and the solubility of the polymer. Tian et al., showed **Poly-18** to exhibit very large specific optical rotations ( $[\alpha]_{435} = -867^\circ$  in toluene,  $-1034^\circ$  in  $\text{CHCl}_3$ ) at room temperature. When annealed at higher temperatures, the specific optical rotation did not approach zero (Fig. 10) [44]. Initially, the specific optical rotation began to decrease but the value plateaus off at approximately  $-360^\circ$ . The  $E_r$  for the initial process was calculated to be 23 kcal/mol but the more interesting observation is the permanent asymmetry that is exhibited by the polymer. It was concluded that a higher level of non-racemizable asymmetry is built into the polymer system as a result of the bulky substituted phenyl pendant groups. Their close packing along the polymer chain prohibits the ability to undergo concerted rotations which removes a level of cooperativity required for full racemization.

**Poly-19** also requires a chiral catalyst (**Cat-7**) to obtain an excess helical sense and racemization through annealing requires over 100 h at  $80^\circ\text{C}$  in toluene (Fig. 11) [42]. The  $E_r$  was calculated as 36 kcal/mol, the highest  $E_r$  reported for a polycarbodiimide from an achiral monomer to date. **Poly-19** was shown to racemize completely and no permanent asymmetry was found to persist. However, as will be discussed in Section 2.5, this polymer revealed some other asymmetric properties of significant importance. Collectively, **Poly-18** and **Poly-19** reveal that very robust and static helical polycarbodiimides can be achieved through helix-sense-selective polymerization of achiral monomers. The next section will focus on unique techniques used for combining dynamic and static helical polycarbodiimide backbones.

### 2.2.3. Miscellaneous helicity experiments

The incorporation of a chiral stereocenter in the  $\gamma$ -position of **Poly-21(R)** and **Poly-21(S)** (Scheme 5) was performed to experiment with the induction of excess helical sense through annealing. It was proposed that combining the bulky 1-anthryl substituent with a configurationally chiral alkyl substituent could lead to a polymer which exhibits a robust and thermally stable helical backbone even if an achiral catalyst is used. Instead of having to

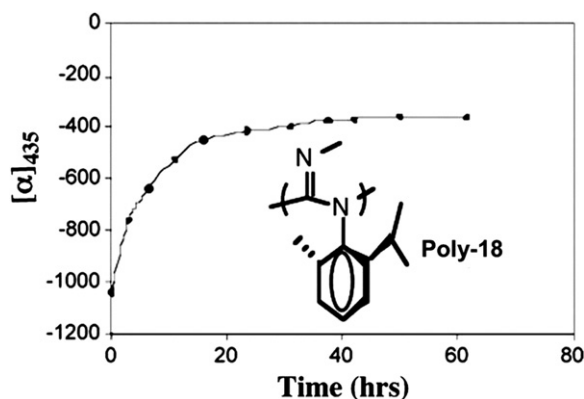


Fig. 10. Annealing of **Poly-18** in chloroform ( $c = 0.33$  g/100 mL) at  $50^\circ\text{C}$  results in initial racemization but not complete racemization. The optical rotation values plateau at  $-360^\circ$  showing a permanent asymmetry related to this polymer system. (Copyright 2004 American Chemical Society, reprinted with permission) [44].

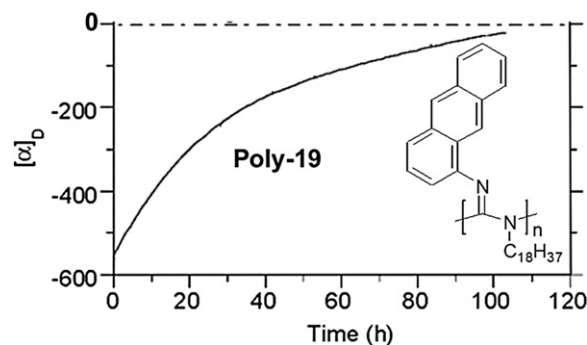
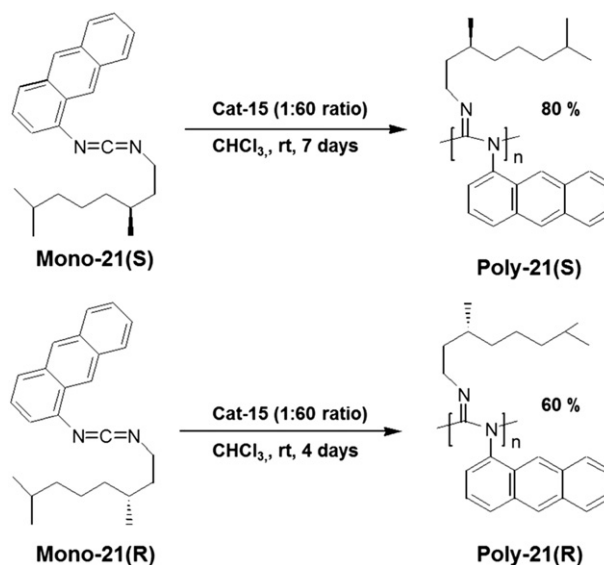


Fig. 11. Annealing of **Poly-19** in toluene at  $80^\circ\text{C}$  requires more than 100 h for full racemization. (Copyright 2005 American Chemical Society, reprinted with permission) [42].

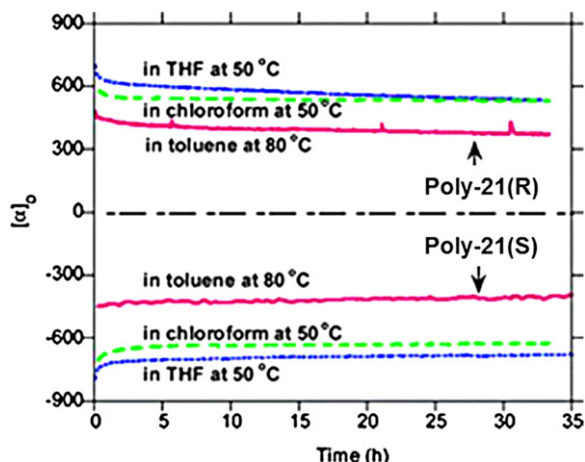
anneal the KCC of **Poly-21(R)** and **Poly-21(S)** into an excess helical sense (TCC), it was discovered that the KCC and TCC are the same for these polymer systems. In other words, the virgin polymers exhibited a large specific optical rotation prior to annealing and it remained stable even at higher temperatures (Fig. 12) [46]. It was concluded that these polymers adopt the thermally preferred helical diastereomer during polymerization when using an achiral catalyst and success was achieved for obtainment of very stable helices even at high temperature. Such a synergistic approach to these polymer systems offers potential utility toward applications in novel liquid crystalline materials and chiral stationary phases (CSPs) for HPLC.

### 2.3. Pendant group influence on properties of polycarbodiimides

As previously mentioned, polycarbodiimides have a remarkable advantage over polyisocyanates and polyisocyanides due to the incorporation of two pendant groups per repeat unit. These pendant groups do not have to be the same and this allows our research to employ a number of synthetic strategies when deciding on the pendant groups used. For example, one pendant group can be chosen to perform a function while the other pendant group can be used solely to improve the desired solubility of the polymer. Due to this synthetic freedom, a number of polycarbodiimides have been synthesized to fully utilize this advantage and obtain desired properties of the polymer system.



Scheme 5. Chiral carbodiimides containing a 1-anthryl pendant group polymerized using achiral (**Cat-15**) catalyst.



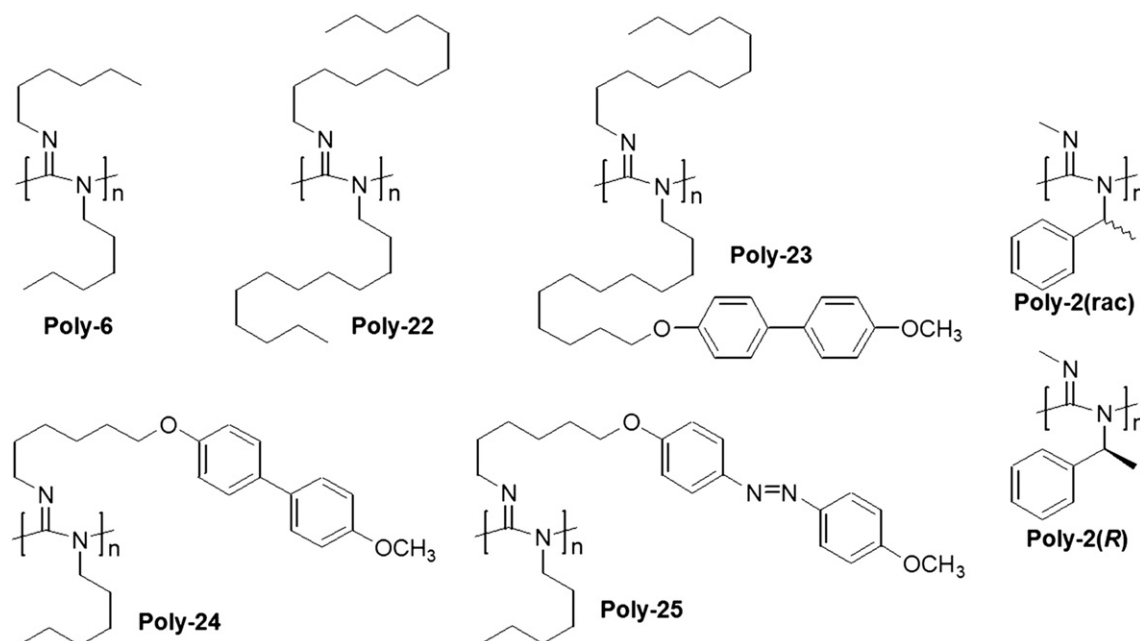
**Fig. 12.** Annealing **Poly-21(R)** and **Poly-21(S)** at high temperatures in various solvents resulted in no significant change in optical rotation suggesting very stable helices and their KCC and TCC are the same. (Copyright 2004 American Chemical Society, reprinted with permission) [46].

### 2.3.1. Liquid crystalline polycarbodiimides

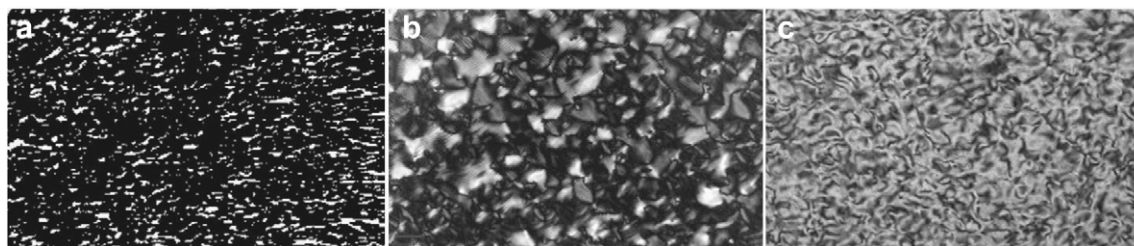
One of the interests in creating stable static helical polycarbodiimides is the application that rigid-rod like polymers have in the field of liquid crystalline (LC) materials. Chiral helices that behave as rigid rods can form cholesteric LCs capable of exhibiting brilliant colors. Other forms of LC behavior such as nematic or smectic phases may be achieved from rigid but racemic polycarbodiimides. Kim et al. first synthesized a variety of polycarbodiimides to better understand their LC behavior [111–113]. Initial investigations were performed on racemic, homochiral and achiral monomers polymerized by achiral **Cat-3** (Fig. 13). A lyotropic LC of **Poly-6** was found to exhibit a layered, smectic mesophase at critical concentration, 20% w/w in toluene (Fig. 14a) [113].

The smectic order of these LC systems is greater than the nematic mesophase shown for polyhexylisocyanate and was attributed to the increased density of identical hexyl pendant groups which provide a uniform corona of aliphatic spacing

between polymer chains. When disrupting the uniformity of the side chains, such as **Poly-2(rac)**, the lyotropic LC (20% w/w in toluene) retains an orientation order but loses the positional order, resulting in a nematic LC phase [112]. Due to the homo-chirality of the side chains of **Poly-2(R)**, this polymer was capable of adopting an excess helical sense and exhibited a cholesteric mesophase from a 12.5% w/w solution in chloroform (Fig. 14b). Since **Poly-2(R)** requires less concentration of polymer to obtain the LC phase, this is an indication that this polymer is stiffer than its racemic counterpart **Poly-2(rac)**. Due to the rigid stable helix and promising LC phase created by **Poly-2(R)**, it has recently been researched and reported by Reggeli et al. as sufficient chiral orientation media for organic compounds [114]. The addition of mesogenic biphenyl (**Poly-24**) and azo-biphenyl (**Poly-25**) side chains could allow the observation of smectic ordering from polycarbodiimides comprised of dissimilarly sized pendant groups. **Poly-24** was found, through X-ray diffractometry, to be a very ordered crystal structure in the solid state with inter-chain distances less than those observed for **Poly-6**. This indicates that the mesogenic side chain actually promotes interpenetration of the coronas surrounding the polymer backbones. As a consequence, LC properties of **Poly-24** were unable to be performed due to poor solubility. **Poly-25** has significantly less order in the solid state and the azo-biphenyl mesogen was soluble and capable of forming a lyotropic LC at 21.4% w/w in 1,1,2,2-tetrachloroethane at 65 °C. It was discovered that the LC of **Poly-25** still retained a nematic structure, concluding that the backbone dominates the phase behavior over the mesogenic side chains (Fig. 14c) [112]. The larger dodecyl pendant group containing polymers, **Poly-22** and **Poly-23** were synthesized to investigate any thermotropic LC properties that may be associated with these systems. Polycarbodiimides have moderate thermal stability but will decompose back into carbodiimides at temperatures upwards of 150 °C. Therefore the idea of surrounding the polycarbodiimide chains in a paraffin-like sea of aliphatic pendant groups, which show melting around 33 °C, may allow the observation of thermotropic LCs at relatively low temperatures. Differential scanning calorimetry (DSC) of **Poly-22** reveals a second endothermic transition around 102 °C which was found to be the formation of a thermotropic mesophase (Fig. 15). **Poly-23**, which contains



**Fig. 13.** Polycarbodiimides studied for liquid crystalline properties.



**Fig. 14.** Optical polarizing microscope images of LC (a) smectic **Poly-6**, 20% w/w in toluene at 45 °C (200×) [115], (b) cholesteric **Poly-2(R)**, 12% w/w in  $\text{CHCl}_3$  at r.t. (500×) [112], and (c) nematic **Poly-25**, 21.4% w/w in 1,1,2,2-tetrachloroethane at 65 °C (200×) [112]. (Figure (b) and (c), Copyright 2004 American Chemical Society, reprinted with permission).

a mesogenic side chain, was found to form a smectic mesophase at 130 °C. Therefore, oppositely to a lyotropic LC, thermotropic ordering is governed more by the mesogenic side chains over the backbone [111]. Zhang et al. synthesized remarkably colorful birefringent cholesteric polycarbodiimide gels by copolymerizing **Mono-2(R)** with a small amount of dicarbodiimide crosslinker (**Mono-26**) (Fig. 16) [115]. Since this polymer contains no chromophores capable of absorbing in the visible spectrum, the colors are produced solely by the Bragg reflection of light from the pitch of the frozen cholesteric domains.

**2.3.1.1. Water soluble polycarbodiimides.** Solubility is a constant synthetic challenge when designing polycarbodiimides. The incorporation of long aliphatic chains onto carbodiimides often relieves some of the inter-chain packing that would otherwise render a polycarbodiimide insoluble in most organic solvents. A majority of the polycarbodiimides discussed up to this point, unless otherwise noted, have exhibited solubility in organic solvents ranging from mid-polarity (THF,  $\text{CHCl}_3$ ) to low-polarity (toluene, cyclohexane). Only a small portion of polycarbodiimides have been synthesized and found to be soluble in higher polarity solvents such as methanol and water. Li et al. was capable of synthesizing a small group of polycarbodiimides which exhibited solubility in such solvents (Fig. 17) [116]. Since biological systems are aqueous, the fruition of hydrophilic polycarbodiimides is important, allowing potential future research pathways, such as biomimetic applications, to be plausible for polycarbodiimide systems.

Often for these systems, their solubility in polar media can be greatly improved by methylation of tertiary pendant group nitrogens using methyl iodide reagent. This technique can be applied to polycarbodiimides that are borderline insoluble in water in order to

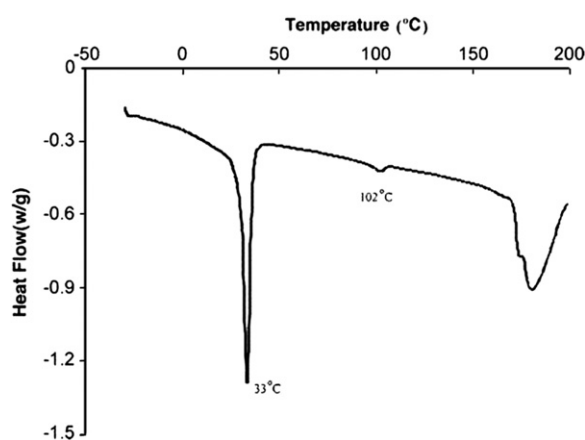
give them the added polarity necessary to become soluble. Such is the case for **Poly-31** (Scheme 6) which is not found to be soluble in water until the piperazine phenyl substituent is methylated [117].

**2.3.1.2. Pendant groups for asymmetric catalysis.** Due to the helical scaffolding upon which these pendant groups are attached, one feasible use for these polymer systems is materials for asymmetric catalysis. Any chemistry that can be performed within an appropriate proximity to the chiral helical backbone may result in stereoselective reaction products [118–122].

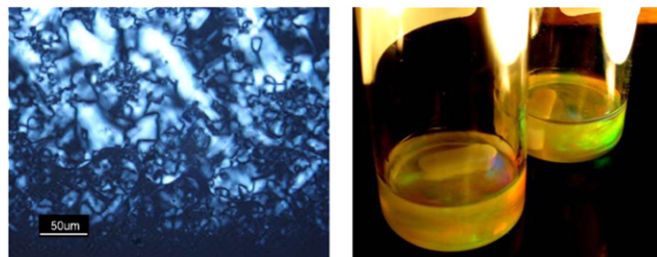
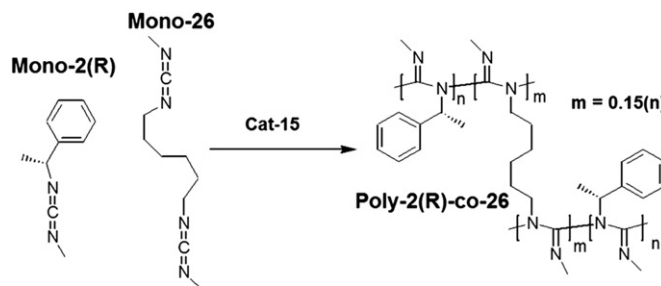
Recently, Budhathoki-Uprety et al. have reported progress toward this concept with the successful synthesis of pyridine pendant group containing polycarbodiimides (**Poly-(32–34)**, Fig. 18) [123]. The pyridinyl heterocyclic nitrogen lone pair functions as a site upon which chemistry may be performed and this was shown through nitrogen–borane coordination using  $\text{BH}_3 \cdot \text{Me}_2\text{S}$ . This new borane-coordinated polycarbodiimide system successfully reduced select aldehydes and ketones [123]. Current work is in progress to assess the stereoselectivity of such reactions.

## 2.4. Regioregularity of polycarbodiimides

Non-symmetric carbodiimide monomers can result in polycarbodiimides containing different regioisomers dependant upon the resulting connectivity or positioning of the monomer pendant groups on the polymer chain (Fig. 19). We refer to these differences

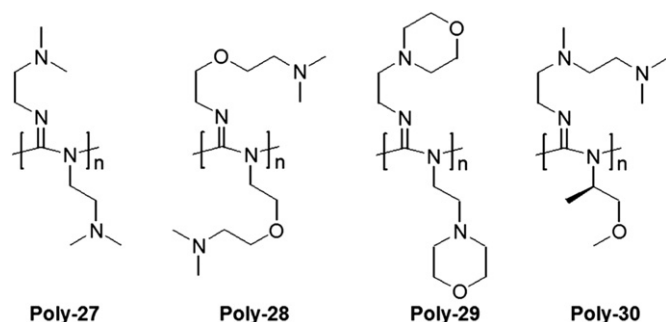


**Fig. 15.** Differential scanning calorimetry (DSC) thermogram of **Poly-22** showing a thermotropic LC phase formation at 102 °C (Copyright 2004 American Chemical Society, reprinted with permission) [112].



**Fig. 16.** Copolymerizing a dicarbodiimide crosslinker (**Mono-28**) with chiral **Mono-2(R)** results in a “locked-in” cholesteric gel [115].



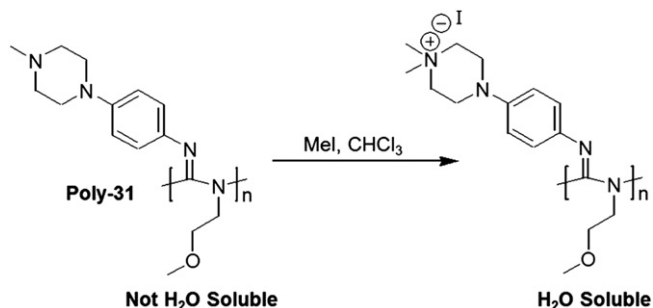


**Fig. 17.** Polycarbodiimides containing high polarity pendant groups enabling water solubility.

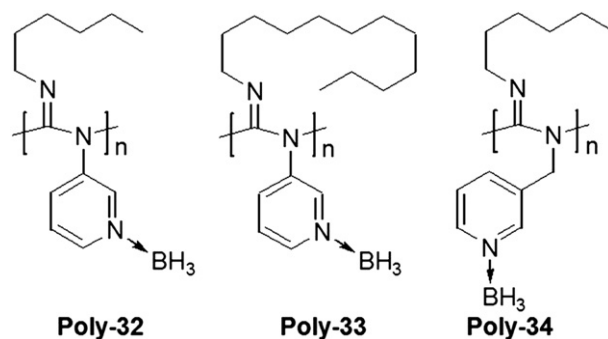
as the regioregularity or regioirregularity depending upon the resulting order. Regioirregularity does not apply to symmetric polycarbodiimides which contain two identical pendant groups since there is no difference between the resulting regioisomers.

By looking further into the mechanism of propagation for these polymer systems, we can deduce that the resulting regioregularity of polycarbodiimides is dictated by the mode of monomer insertion on the amidinate-titanium(IV) active chain end (Scheme 7). Because of this, we do not expect very similar pendant groups, such as *n*-heptyl versus *n*-hexyl, to have a dominant mode of monomer insertion. Oppositely, if the two pendant groups are significantly different based on electronic or steric effects, the resulting regioregularity of the polycarbodiimide may be high and may favor one regioisomer over the other. To accurately determine the polycarbodiimide regioregularity, two facts must be known; how much of a preferred regioisomer is present and which regioisomer it is (i.e. what pendant group lies on the imine or amine position). Ever since the discovery of polymerizing carbodiimide monomers in a living fashion by our research group, it has been with great interest to develop ways of controlling and analyzing the regioregularity of these polymer systems. Over the last decade, as the complexity of polycarbodiimides has increased, this macrostructural assessment has warranted even more attention. Even today, a definitive way to accurately quantify the regioregularity of polycarbodiimides eludes us, although some progress had been made.

NMR spectroscopy, although a key contributor to many microstructural determinations for other polymers and a very powerful analytical technique, is still in need of more investigation before any significant conclusions can be developed about the regioregularity of polycarbodiimides. This lies mostly due to the slow relaxation times of the backbone carbons and significant broadening of pendant group atoms near the vicinity of the backbone due to anisotropic effects. Current research in our group is investigating



**Scheme 6.** Aqueous solubility can be induced through methylation of polycarbodiimide pendant groups [117].



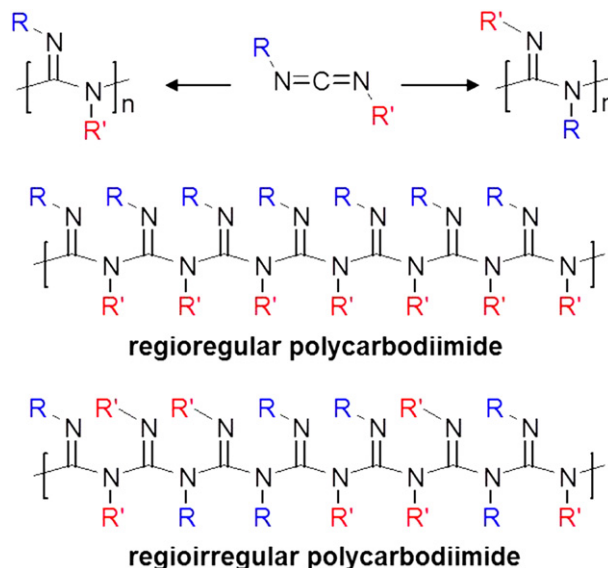
**Fig. 18.** Pyridinyl pendant group containing polycarbodiimides can coordinate to borane and be used as potential sites for asymmetric stereoselective reduction of aldehydes and ketones [123].

<sup>15</sup>N labeled polymer systems with hopes of unlocking new NMR structural information techniques.

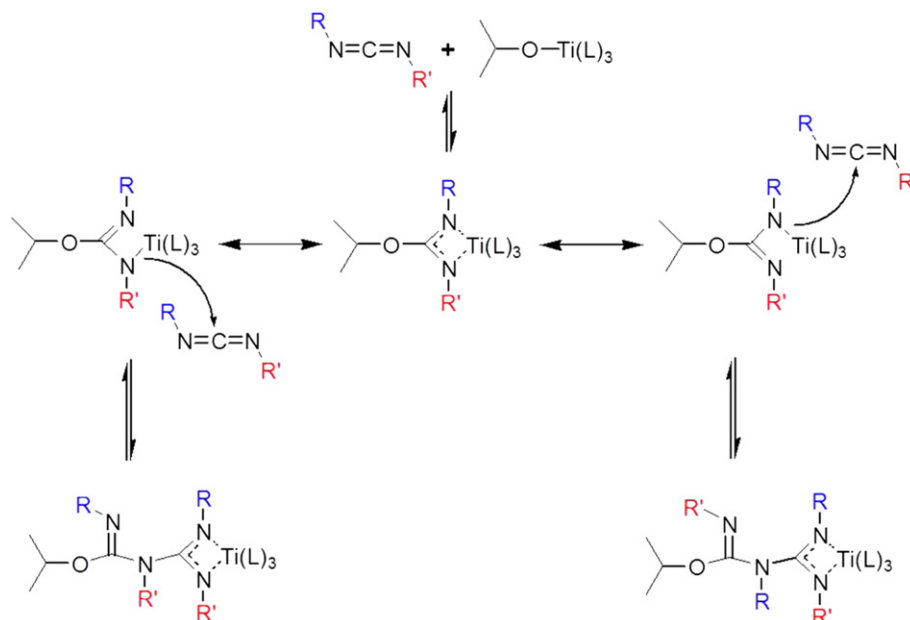
Only a few methods for determination of polycarbodiimide regioregularity have been reported thus far and all of them utilize infrared spectroscopy (IR) as a means of observing different C=N imine stretch absorptions along the polycarbodiimide backbone. It was theorized that polycarbodiimides with sufficiently different pendant groups, such as alkyl versus aryl would result in two different energy imine absorptions observable by IR if regioirregularity is present. Recent research has proven this initial assessment to be incorrect and fluctuations of imine absorption energy maxima can be seen through solution IR at various temperatures [124]. It is now hypothesized that symmetry elements associated with the helix are playing a key role toward multiple infrared imine absorptions observed.

## 2.5. Static helical polycarbodiimides with reversible dynamic properties

A majority of the recent publications on polycarbodiimides have dealt with a very unique reversible conformational switching behavior that was initially discovered for *N*-(1-anthryl)-*N'*-(*n*-octadecyl) polycarbodiimide, **Poly-19** (Fig. 20) [42].



**Fig. 19.** Regioregular outcomes for asymmetric carbodiimide monomer polymerizations.



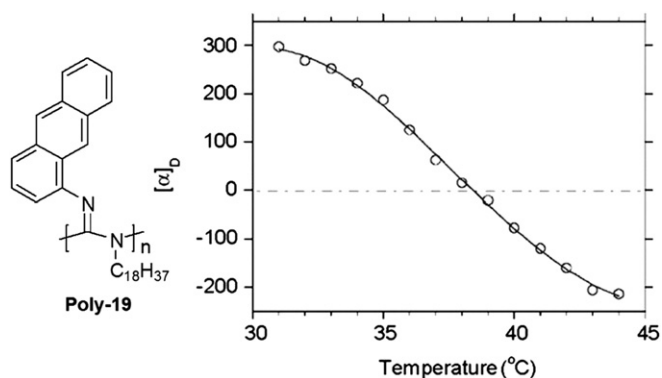
**Scheme 7.** Mechanism for carbodiimide monomer initiation and propagation on titanium(IV) amidinate complexes and the resulting regioisomers.

After further chiro-optical investigations using electronic circular dichroism (ECD) and vibrational circular dichroism (VCD), it was concluded that these large conformational changes are not due to helical reversals, but instead result from realignment of the restricted anthryl pendant groups around the static helical polycarbodiimide backbone scaffold [45]. Due to their size and asymmetry, the polyarene groups cannot freely rotate and hence their alignment forms a secondary order of conformational chirality around the helix. The repositioning of these arene groups, believed to be caused by differences in energy states between the dipole of the arene substituent and the inherent dipole of the polycarbodiimide backbone, allows for the observation of dramatic chiro-optical changes (Fig. 21). **Poly-19**, although novel, was limited by only exhibiting such behavior in toluene. Dramatic changes in specific optical rotation were not observed for **Poly-19** in any other solvents tested.

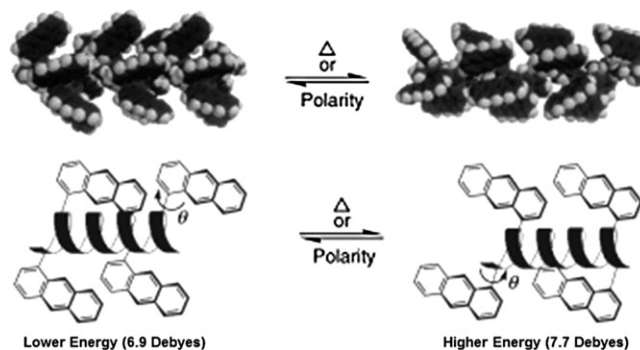
Kennemur et al. has synthesized and reported a library of non-symmetric aryl–alkyl polycarbodiimides designed to probe the governing forces behind this unique behavior (Fig. 22) [48,49]. The initially designed **Poly-35** broke through aforementioned

limitations as large changes in optical rotation are observed in various solvents (Fig. 23) [48]. Given this new observation, it can now be concluded that solvent plays a large role on the energy required for these conformational changes. It was also concluded that these changes in observed optical rotation are not due to aggregation of polymer chains.

Variable temperature ECD is shown for **Poly-35** in Fig. 23 and the repositioning of the arene chromophores can be seen by reversals in observed Cotton effects over the respective switching temperature range in THF. Another interesting discovery for these systems is that the optical rotation outputs for **Poly-35** can be held constant by holding the solution temperature isothermal anywhere within the conformational switching profile. This can be seen in Fig. 24 where the polymer solution in THF was held at different temperatures with relative stability during 4 h increments. Such a behavior allows consideration of these polymer systems as tunable polarization materials. Reducing the alkyl chain length (**Poly-35** versus **Poly-36**) revealed no changes in the conformational switching behavior leading to the conclusion that this pendant group serves only to improve solubility of these polymers [48].



**Fig. 20.** **Poly-19** was discovered to undergo large reversible changes in specific optical rotation at relatively low temperatures in toluene ( $c = 0.10$  g/100 mL). (Copyright 2005 American Chemical Society, reprinted with permission) [42].



**Fig. 21.** Theoretical models for the two anthracene pendant group rotational states. The geometries of both states were determined by optimization of the repeat unit at the semi-empirical level (AM1) and then optimization of the 18-mer at the molecular mechanics level (MMFF94) (Copyright 2005 Wiley–VCH Verlag GmbH & Co. KGaA. Reproduced with permission.) [45].

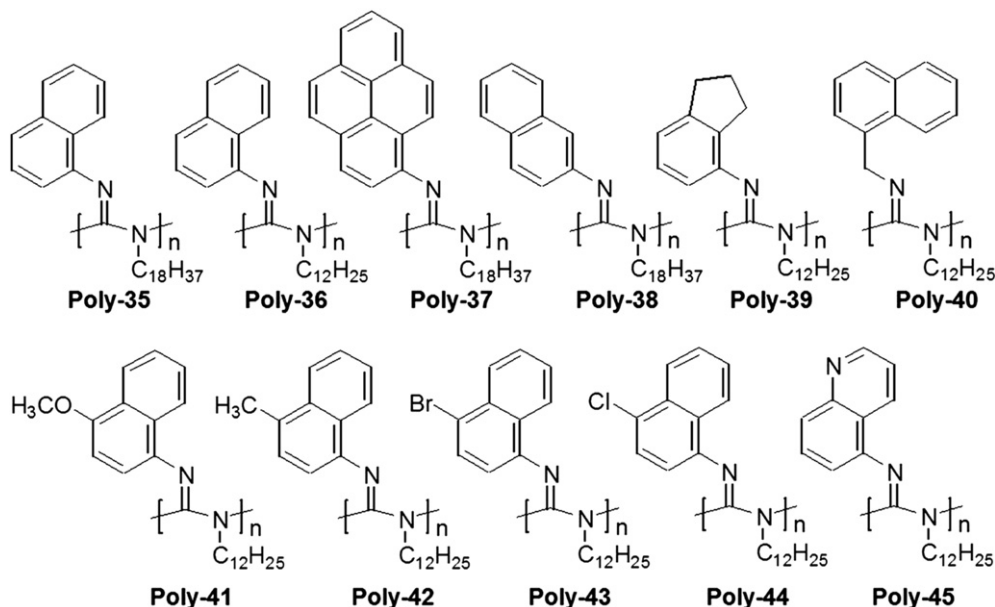


Fig. 22. Synthesized library of non-symmetric aryl–alkyl polycarbodiimides designed for investigation the reversible conformational switching properties.

Increasing the size of the aryl pendant group led to the discovery that the larger 1-pyrenyl pendant groups on **Poly-37** exhibit higher amplitude of specific optical rotations but the conformational changes are considerably broadened and require much higher energy when compared to **Poly-35** [48]. A sub-series of polymers were also designed to investigate the importance of spatial arrangement (**Poly-38**), complete aromaticity (**Poly-39**), and connectivity (**Poly-40**) of the arene pendant group. Interestingly, none of these polymers were found to exhibit any significant

changes in optical rotation throughout the respective temperature ranges in any solvents tested [48,49].

The quenching of this chiro-optical behavior by these small synthetic deviations is a testament to the delicate ballet of non-covalent interactions and steric restrictions necessary to allow these conformational changes to be observed. Further synthetic investigations were focused on substituent effects placed on the parent 1-naphthyl pendant group and how such substituents would change the energy of these systems to undergo these

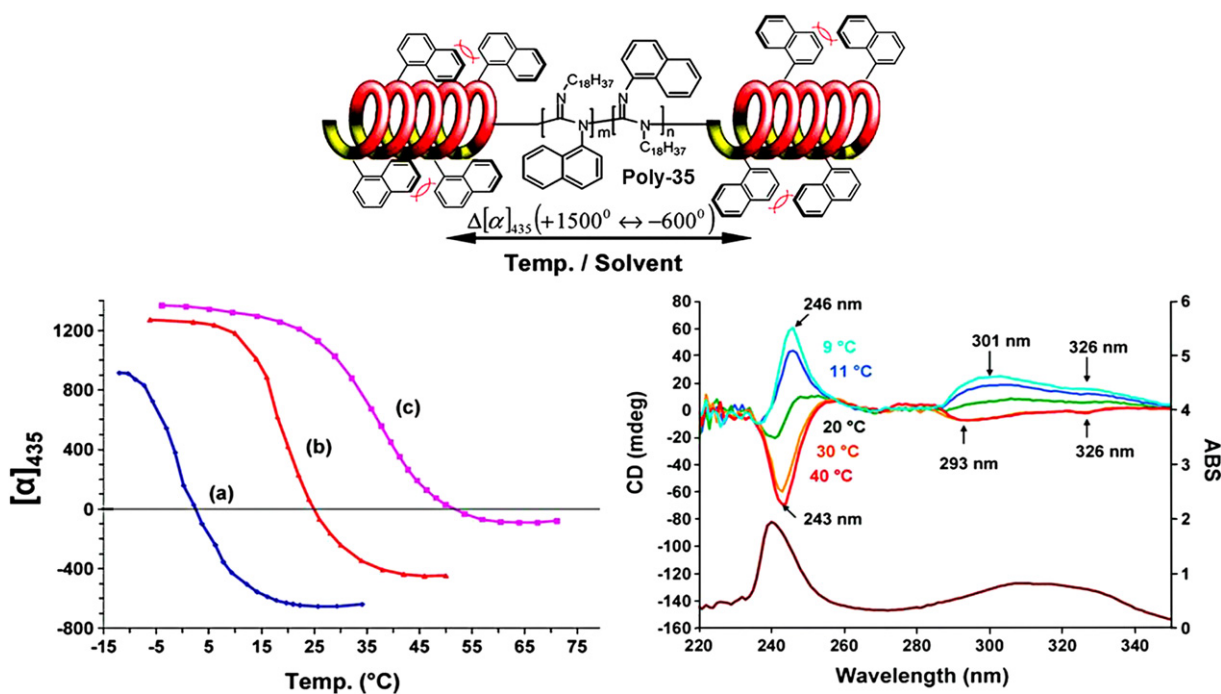


Fig. 23. [top] Synthesis of **Poly-35** resulted in a more versatile static helical polycarbodiimide with reversible dynamic properties and higher amplitude of chiro-optical response. [bottom-left] Variable temperature polarimetry of **Poly-35** in (a)  $\text{CHCl}_3$ , (b) THF, and (c) toluene ( $c = 0.20\text{--}0.22$  g/100 mL). [bottom-right] ECD of **Poly-35** in THF at various temperatures ( $c = 40$   $\mu\text{g/mL}$ ). (Copyright 2010 American Chemical Society, reprinted with permission.) [48].

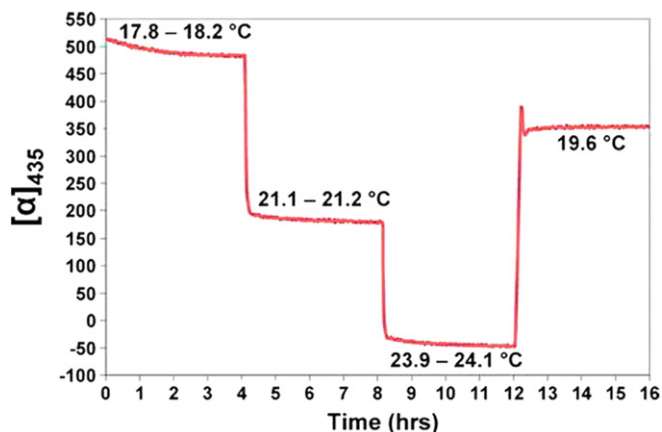


Fig. 24. –Specific optical rotation of **Poly-35** in THF held isothermal at four different temperatures during 4 h increments ( $c = 0.200$  g/100 mL). (Copyright 2010 American Chemical Society, reprinted with permission.) [48].

observed conformational changes. Electronic or dipolar alterations were designed by the incorporation of functional groups onto the 4 position of the naphthalene unit (**Poly-41–44**) and by heteroatom replacement of an arene carbon (**Poly-45**). Through these electronic perturbations, drastic changes in the required energy for these conformational changes are observed with respect to solvent (Fig. 25). Although we do not observe any correlation between the substituent sigma values and the energies at which these conformational changes occur with respect to each solvent, these results further enforce our beliefs that underlying governance for this behavior lies within complex aromatic–aromatic and aromatic–backbone interactions as well as polarity effects. For all of the aforementioned switching polymers, kinetic data have not been obtained due to the extreme speed with which these conformational changes occur; they happen faster than our current instrumentation can record them.

To our knowledge, these helical polycarbodiimides are the only systems reported to undergo large reversible changes in optical rotation (which also change in sign of rotation) without helical inversions [35,76,125–128], aggregation [129], or the influence of chiral stimulant such as configurationally chiral pendant groups, chiral guest molecules, or chiral solvent [130–137].

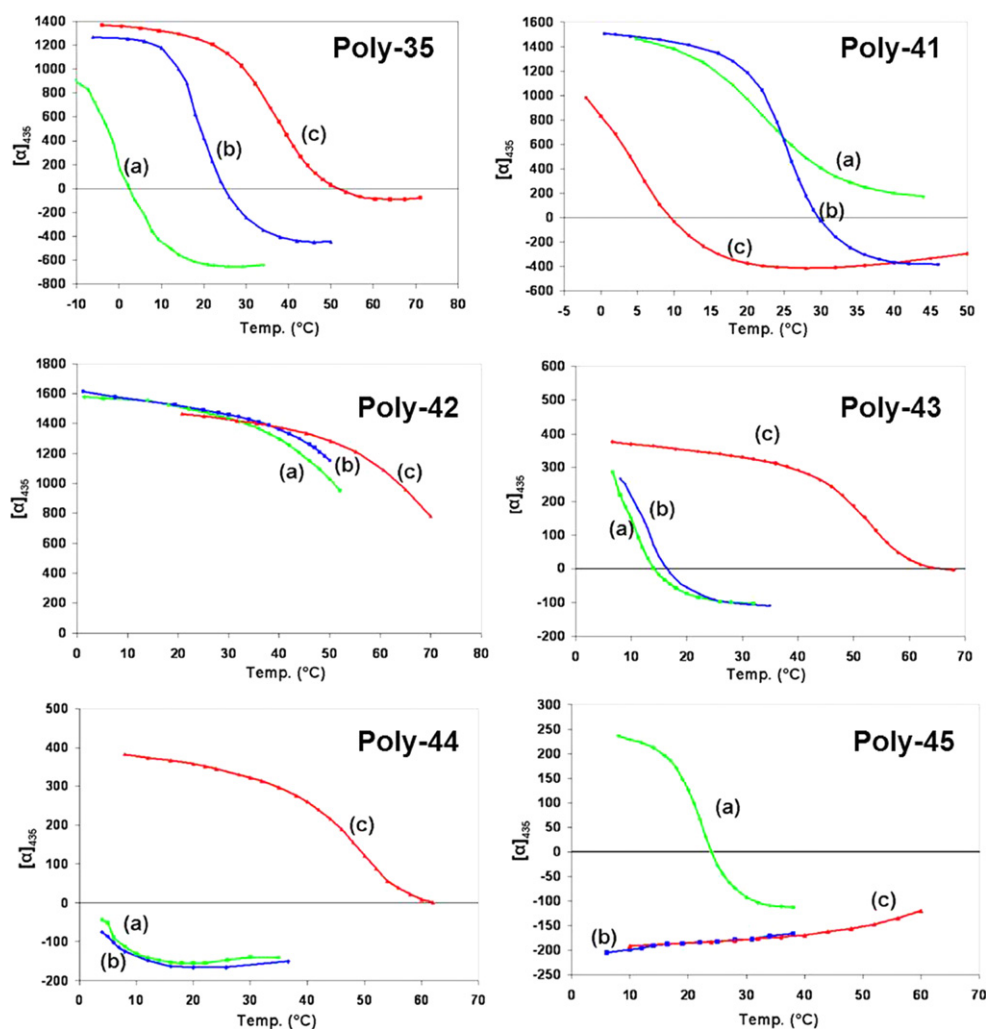


Fig. 25. Variable temperature polarimetry of **Poly-41–45** showing dramatic conformational switching energy differences between each polymer with respect to solvent and when compared to the parent unsubstituted **Poly-35**. For each plot, the polymer was tested in (a)  $\text{CHCl}_3$  green (b) THF blue and (c) toluene red. Specific optical rotations were recorded within respective temperature ranges for each solvent using 435 nm light and a concentration range of 0.20–0.22 g/100 mL. (Copyright 2010, Wiley-VCH, reprinted with permission).



### 3. Conclusions and future outlook

Polycarbodiimides represent a unique and versatile class of functional chiral polymers capable of exhibiting a large variety of properties due to the inherently customizable synthesis of their carbodiimide monomer precursors. They can be synthesized to exhibit solubility in everything from hexane to water and their potential utility encompasses biomimetic materials, liquid crystals, sites for asymmetric catalysis, optical display materials, chemo-sensory materials, and tunable polarizers. Combining the chiral helical structure with the inherently basic nitrogen rich backbone presents utility for these materials for selective absorbency and chemical recognition through acid–base interactions. Additionally, these systems exhibit very interesting levels of asymmetry which stems from the helical backbone and is projected into dynamic secondary coronas of conformational chirality. Conformational changes of these secondary levels of asymmetry have revealed unique low-energy reversible expressions of asymmetry. Although many strides have been taken to further understand the complexity of these systems, it is still an ongoing task, and it is felt that the full utility of these systems are yet to be realized. It is believed that the research presented in this manuscript constitutes a strong fundamental foundation for the continued exploration of these systems. As macromolecular and supramolecular chiral order is further understood, so will the possibilities of polycarbodiimides for frontier application.

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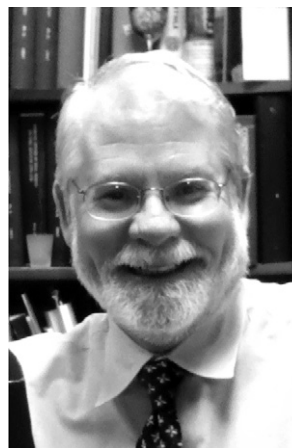
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**Justin G. Kennemur** obtained his B.S. Emphasis Degree in Chemistry from Radford University in 2002 and received his Ph.D. in Synthetic Helical Polymer Chemistry from North Carolina State University under the direction of Bruce M. Novak in 2010. Between 2002 and 2005 he worked as an Analytical Polymer Chemist at Polymer Solutions Incorporated in Blacksburg, VA. In May 2010, he was awarded the ACS Richard D. Gilbert Award in Polymer Science and will receive the 2010 AkzoNobel Student Award in Applied Polymer Science at the Spring 2011 National ACS Meeting in Anaheim, CA. He will begin post-doctoral research in the field of block copolymer materials with Marc Hillmyer at the University of Minnesota – Twin Cities starting in January 2011. His future goal is to become a Principal Investigator in the direction of synthesis, analysis, and catalysis of advanced functional polymer materials.



**Bruce M. Novak** started his college education at California State University, Northridge (CSUN) where he received both BS and MS degrees in chemistry. He then moved to the California Institute of Technology (Caltech), where he did his Ph.D. studies under the direction of Professor Robert Grubbs. Since graduation, his faculty appointments have been at the Chemistry Department, UC Berkeley, Department of Polymer Science and Engineering, UMass, and the Chemistry Department, North Carolina State University. Along with being Department Head at NCSU from 1998 to 2004, he holds the Howard J. Schaeffer Distinguished University Professorship and is an Associate Editor of *Macromolecules*. He has received numerous awards including a Presidential Young Investigator Award, Presidential Faculty Fellowship, Alfred P. Sloan Fellow, ACS Polymer Division Carl S. Marvel Creative Polymer Chemistry Award, and the Alumni Outstanding Teacher Award at NCSU.